The effect of dislocations and chemical environment on the stress-corrosion cracking in face-centered cubic alloys

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AXEL RÖNNQUIST

FIL. LIC., NORRL.

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OF THE UNIVERSITY OF UPPSALA, TO BE PUBLICLY DISCUSSED
IN THE LECTURE HALL OF THE INSTITUTE OF CHEMISTRY,
OCTOBER 20, 1967, AT 10 A.M., FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.
IN ADDITION TO THIS REVIEW THE PAPERS
NUMBERED 1, 2, 3, 4 AND 5 IN THE LIST OF REFERENCES
WILL BE PUBLICLY DISCUSSED.

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The effect of dislocations and chemical environment on the stress-corrosion cracking in face-centered cubic alloys

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INTRODUCTION

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Stress-corrosion cracking is defined as the joint effect of stress and chemical attack, causing brittle failure. If the cracks are formed along the grain boundaries they are called "intercrystalline or intergranular cracks", and if they go through the grains they are called "transcrystalline or transgranular cracks".

The present paper is a summary of the work done in recent years at the Swedish Institute for Metal Research. Parts of the work have been published earlier covering studies of distribution of active sites on the metal surface,[1–3] initiation and propagation of stress-corrosion cracks, their relation to the metal structure and the influence of stacking-fault energy.[4, 5] All the studies have been done on stainless steel or α-brass. Recent work, which is included in the present paper, deals with the effect of applied load, chemical environment and ordering in the alloy. Finally a new model for stress-corrosion cracking is suggested, in which it is assumed that metal complexes formed in the solution cause a decrease in the surface energy of the metal. The model is able to explain metal physical aspects of the process as well as the necessity of having a specific chemical environment.

The first publications definitely dealing with stress corrosion in copper alloys are, according to Rask,[6] from 1906. Rask, who investigated the origins of the expression "season cracking", which is a synonym for stress-corrosion cracking in brass, reported two explanations. One was based on the suggested resemblance to the cracking of wood during seasoning, and one was based on a relation found in India between cracked cartridge cases and the monsoon period. It is reasonable to assume that the monsoon could cause a change in the composition of the air having an accelerating effect on the stress-corrosion process in cold-worked brass.

Stress-corrosion cracks in ductile f.c.c. metals are either transcrystalline or intercrystalline, the chemical environment and the heat-treatment of the alloy being influencing factors. It is typical for austenitic stainless steel to show transgranular cracks in chloride solutions and intercrystalline cracks in nitride solutions. In α-brass stress-corrosion cracks are easily formed by ammoniacal solutions. If the pH is lower than 7, intercrystalline cracks are formed, except in the range pH 4–6, where transcrystalline cracks dominate, as at pH above 7.[7] The characteristics of transcrystalline cracking which must be explained by a final theory are as follows:

1. Brittle failure in a ductile alloy.
2. The formation of transcrystalline cracks in specific environments only.
3. Sensitive alloys fail at stresses far below the fracture stress as determined from a tensile stress-strain curve.

Ever since the introduction of stainless steel, in Sweden in about 1920, the chemical industry has, according to Lindh,[8] had trouble with stress-corrosion cracking in the austenitic steels under specific conditions. However, the first reports dealing with stress-corrosion cracking in steel did not appear until 1940. The historical development of the research work in the field is reflected in the reports from a number of different international and national symposia on stress-corrosion cracking.[9–13]

The first studies of stress-corrosion cracking were made using electrochemical methods. Since about 1956 the electron microscope has been applied to metal research, and also stress corrosion has been studied with the aid of this new tool, which has made it possible to approach the problem from the metal physical point of view. Commonly the literature, when reviewed, is divided into two groups, electrochemical and metal physical work. As a number of recent review articles[14–16] and bibliographies[17–21] are available, only the general ideas of the most relevant theories for stress corrosion will be presented.

EARLIER WORK

The first theory which attempted to describe the stress-corrosion process quantitatively was suggested by Hoar and Hines.[22] Their theory was based on two assumptions: 1) the propagation of the crack is caused only by a pure electrochemical dissolution of the alloy and 2) the anodic dissolution of the alloy is highly affected by the mechanical conditions. Hoar and West[23] showed that when the metal is yielding, strain rates of about 5 % per minute or more reduce the activation polarization of 0.18 V required to dissolve static metal at 0.5 A per cm^2 to a value, not more

than a few mV, experimentally indistinguishable from zero. Such a drastic lowering of the overpotentials required to produce current densities up to 0.5 A per cm^2 was compared with those required for static anodes. However, van Rooyen[24] criticized certain aspects of the measurements made by Hoar and West. In a later paper Hoar and Scully[25] reported similar measurements made using a potentiostatic technique instead of the earlier galvanostatic method. The new results were in good agreement with those reported earlier.

On the bases of these measurements Hines[26] worked out the details in an electrochemical theory, more correctly a mechano-chemical theory. He calculated the potential drop, V, along the depth of the crack and got the expression:

$$V = sk_2\varrho\left[1 - \left\{\frac{i}{2s} - Ik_1^2k_2\right\}\ln k_1^2k_2\right] \tag{1}$$

where ϱ is the specific resistance of the electrolyte within the crack, I the anodic current density on the crack sides, i the current required for propagation of unit length of the advancing edge and s the depth of the crack. The constants k_1 and k_2 are determined by the applied mechanical stress and the effective yield stress in the bottom of the crack.

The characteristic potential E for a propagating crack is expressed by

$$E = V + Vp \tag{2}$$

where Vp is a polarisation factor composed of three terms; activation polarisation at the free metal surface (η_A), the concentration polarisation (η_C), and the polarisation caused by the presence of the surface film (η_F). Hines showed that V is usually negligible and η_A and η_F are reduced through yielding at the bottom of the crack, while η_C largely will be determining the polarisation factor Vp. However, as the crack gets wider, fresh electrolyte is sucked down to the bottom, which reduces η_C.

A crack propagation rate of 0.5 cm/hr has been suggested.[27] This, according to Hines, would cause a current density of 1 A/cm^2, which is regarded as a realistic value.

Hines theory has many interesting points and is based on assumptions which are strongly supported by experimental results. Yet it does not fully explain the obvious relation between the metal structure and the crack-path. It does not even explain the necessity of a specific environment for the formation of stress-corrosion cracks.

Another group of theories are characterized by assuming a mechanical fracture mechanism trigged by electrochemical attacks. In this group are included the theories of Forty[28] and Robertson and Tetelman.[29]

Forty, who studied α-brass in ammoniacal solution assumed that the zinc in the alloy is preferentially dissolved. Due to this reaction vacancies are formed which diffuse, forming voids. The voids will be perfect obstacles for dislocations, and by applying the Fujita-theory,[30] which deals with interactions between voids and dislocations, Forty found that the local strain is high enough to cause a brittle fracture. The crack propagates through the alloy until it hits an active slip plane. A new chemical attack takes place, forming new vacancies and the process just described is repeated.

The theory suggested by Robertson and Tetelman, who studied stress-corrosion cracking of copper–gold alloys in ferric chloride solutions, is based on the Stroh-mechanism[31] for the nucleation of cracks. If an obstacle for dislocation movement is formed in the alloy, dislocation pile-ups will occur. The associated local stress in the alloy is a sum of the stress from each dislocation in the pile-up. If the barrier is strong enough, the dislocation pile-up will finally collapse or a crack in the metal structure will be formed. A crack propagates when the energy

$$S \geqslant \tfrac{1}{2}\sigma n b \qquad (3)$$

where σ is the stress caused by a single dislocation, n is the total number of dislocations in the pile-up, and b the Burgers vector.

Robertson and Tetelman assumed that the chemical reaction with the metal surface causes an energy S_r which lowers the energy necessary for propagating the crack, which will be reduced to S–S_r. They further found that the initiation of the corrosion attack is connected with Cottrell–Lomer barriers.[32] In particular it was suggested that intersecting $\{111\}$ planes containing stacking faults are especially sensitive to an initial attack. In this way a chemically dissolved tube is formed in the [110] direction, making the barrier stronger and allowing larger dislocation pile-ups to be formed. By combining different dislocation types, Robertson and Tetelman calculated the maximum stress vector, which was found to be large enough to cause brittle fracture.

Both these mechanical theories are supported by many metal physical observations. They both explain why a stress-corrosion attack is related to specific crystallographic sites. They also explain why materials with different stacking-fault energy will behave in different ways. However, none of the theories presented above are able to explain the specific effect of the chemical environment.

According to Pickering and Swann,[33] stress-corrosion cracks are formed by tubular attack in an alloy exposed to a solution causing stress-corrosion cracking, while a solution which does not cause stress-corrosion cracking produces a uniform surface roughening. Initiation

TABLE I. *Composition of steels investigated*

Steel	C %	Si %	Mn %	S %	P %	Cr %	Ni %	Mo %	Al %
18.11	0.002	0.007		0.005	0.001	18.0	10.82	< 0.005	0.012
18.11–2P	0.002	0.025		0.002	0.19	18.1	11.00	< 0.005	0.008
18:8 L	0.088	0.43	1.35	0.001	0.003	17.6	8.6	0.46	
10RE21	0.084	0.46	0.50	0.010	0.013	27.0	5.1	1.54	

of a tubular type of attack occurs at grain boundaries, antiphase boundary-junctions, precipitates and other sites which were associated with compositional fluctuations in the surface film. It is further proposed by Pickering and Swann that when susceptible alloys are exposed to corrosive environments, a mechanically weak, pitted structure is produced at active planes and that ductile fracture occurs through this corroded regions. The observed rate of pitting attack can achieve the rate of propagation of stress-corrosion cracks.

In a recent paper Swann and Embury[34] modify the theory to include the effects of surface-film rupture on crack nucleation. An important point in the theory is that it explains some relation between the physical properties of the alloy (as stacking-fault energy and short-range order) and the character of stress-corrosion cracking. Although Swann and Embury have undertaken a lot of work to understand the influence of the environment, their theory is still lacking an explanation of why only specific environments cause stress-corrosion cracking.

EXPERIMENTAL

Specimens

The main work has been done on two stainless steels, 18: 11 and 18: 11-2P, the compositions of which are given in Table I. As can be seen, the level of impurities is very low in these steels, except for the one containing an addition of 0.2% phosphorus. The steels were produced on a laboratory scale, and due to the low carbon content the nickel was raised to 11% to get stabilization of the austenitic structure.

Additional work was done on a commercial austenitic steel 18: 8 L and some work has also been carried out on a ferritic-austenitic stainless steel 10RE21. Finally, as a comparison, commercial α-brass (70% Cu, 30% Zn) SM1070 was studied. In all cases the specimens were machined from the metal as received in sheets 1 mm thick.

The standard heat treatment of the steel specimens comprised heating for 1 hour in evacuated silica tubes at 1050°C and then water quenching.

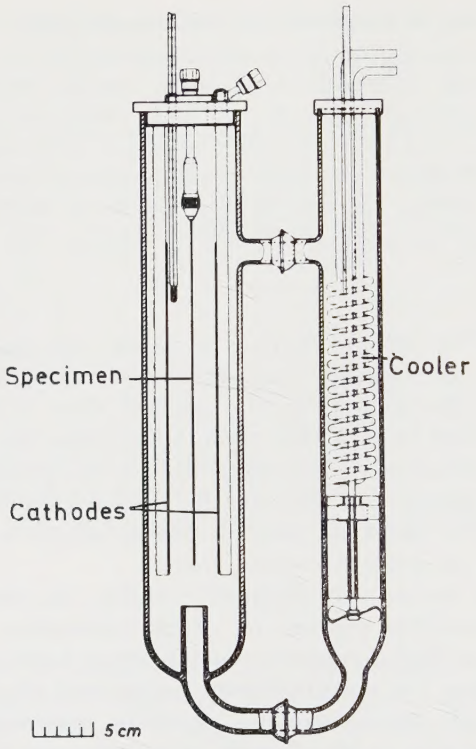

Fig. 1. Apparatus for electrolytic polishing.

The α-brass was heat-treated in a similar way but at 550°C. The 10RE21 steel was heated at 970°C for $^1/_4$ hour.

Before the specimens were exposed to the stress-corroding environment they were electrolytically polished and stored for 24 hours in a desiccator. The polishing apparatus is shown in Fig. 1 and the polishing conditions are given in Table II.

Corrosion cell

Two different designs of corrosion cells were used. The first one, described earlier,[5] was made for specimens in the form of strips $5 \times 300 \times 1$ mm. In this cell the specimens were loaded in a vertical position. A disadvantage of this arrangement was due to the phase boundary between liquid and air surrounding the specimen inside the glass-vessel. The corrosion attack often appeared close to this boundary. To avoid this a new cell was constructed allowing for a horisontal specimen position as seen in Fig. 2. In this new cell specimens with a gauge length

TABLE II. *Conditions for electrolytic polishing*

Material	Treatment of machined specimen	Electrolyte	Polishing conditions
Steel	Annealed at 1050°C, 1 h	70% ethanol 12% butylglycol 8% perchloric acid 10% water	18 V, 4 min
Brass	Annealed at 550°C, 1 h	1025 g o-phosphoric acid 500 g ethanol 500 g water	1.75 V, 15 min

were used. With this design the maximum stress was obtained in the part of the specimen which was placed in the middle of the cell and wholly surrounded by the liquid.

Preparation of solutions

In the case of steels, solutions with a magnesium chloride content of 32% were used, and during the test a slow stream of oxygen was bubbled through the solution.

To accelerate the stress-corrosion process, some tests were carried out with $FeCl_3$ added to the magnesium chloride solution. The magnesium chloride content was then adjusted to maintain a constant concentration of chloride ions.

α-brass was tested in an ammoniacal solution containing copper sulphate. This solution was prepared as described by Mattsson.[7] In all cases chemical compunds of *pro analysi* purity, delivered by Merck AG, Darmstadt, were used.

Microscopic investigations

Different microscopic techniques were used to study the specimens before and after testing. Early stages of the stress-corrosion process were studied by electron microscopy, and later stages by optical microscopy.

After exposure in the corroding environment the specimens were washed in *aq. dest.* and rinsed in ethanol. Due to the favourable shape of the specimens in the form of strips it was now possible to make replicas of the surface without further preparation. By using an extraction replica technique as described by Modin and Modin,[35] the distribution of active sites on the metal surface could be studied (in an RCA EMU-2 microscope) as they were decorated by the solid corrosion

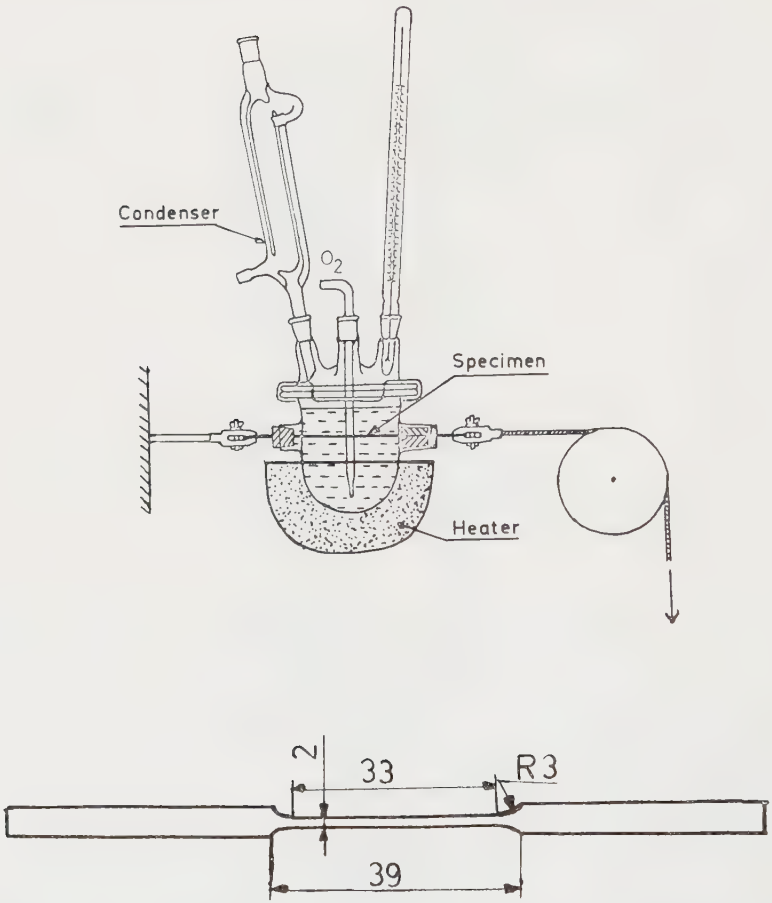

Fig. 2. Stress corrosion cell (above) and specimen dimensions in mm (below).

products, which could be easily extracted. By making a second replica of the same area the relation between the sites for chemical attack and the metal structure on the surface could be studied.

For transmission studies in the Philips EM 200 electron microscope thin foils of the metal were prepared by electrolytic thinning. The polishing conditions for the different materials and the composition of the electrolytes used are given in Table III. For the purpose of determining stacking-fault energies, the metal was thinned down from both sides, but for studying specimens attacked by the stress-corrosion process the metal was thinned down from one side only. This was achieved by covering one of the sides by a lacquer.[3] The thinning was done using a modified Bollman technique.

TABLE III. *Conditions for electrolytic thinning*

Material	Electrolyte	Voltage
Steel	60% o-phosphoric acid 40% sulphuric acid	7–8 V
Brass	1025 g o-phosphoric acid 500 g ethanol 500 g water	1.60 V

Optical microscopy was used to study the structure of the alloys and the stress-corrosion attack, the latter by using a contrast technique[36] to observe the slip traces. As the surface finish after the electrolytic polishing was well suited to optical microscopic observations these were done directly after the exposure to the corroding environment. As a rule the surface finish was not badly destroyed by the general corrosion, except in the case of α-brass, which was often covered by a rough layer of corrosion products.

Stress-corrosion cracks were studied also after systematic grinding of the specimen to allow for a step-wise study of the crack from the surface down to the bottom.

Fractographic studies

Replicas from surfaces of stress-corrosion cracks were studied in the electron microscope (RCA EMU-2) but the interpretation of the electron micrographs was not easy, due to disturbances from small amounts of corrosion products.

A much more favourable technique was the study of fracture surfaces using a Cambridge Stereoscan electron microscope.[37] As this type of microscope is a relatively new one, a block diagram of the basic operating principles is given in Fig. 3.

A primary beam of electrons from a heated tungsten filament is focused on a specimen and made to scan the surface by scanning coils. Electrons liberated from the specimen by the probe are detected by a scintillator photomultiplier system, the resulting signals being used to modulate the brightness of a cathode ray tube screen which scans in synchronism with the electron probe scanning the specimen. Magnifications obtainable vary between 50 and 100,000 times, but maximum useful magnification is usually between 20,000 and 30,000 times. The resolution depends upon the diameter of the electron probe and of course upon the type of specimen. It is possible to obtain a resolution which is

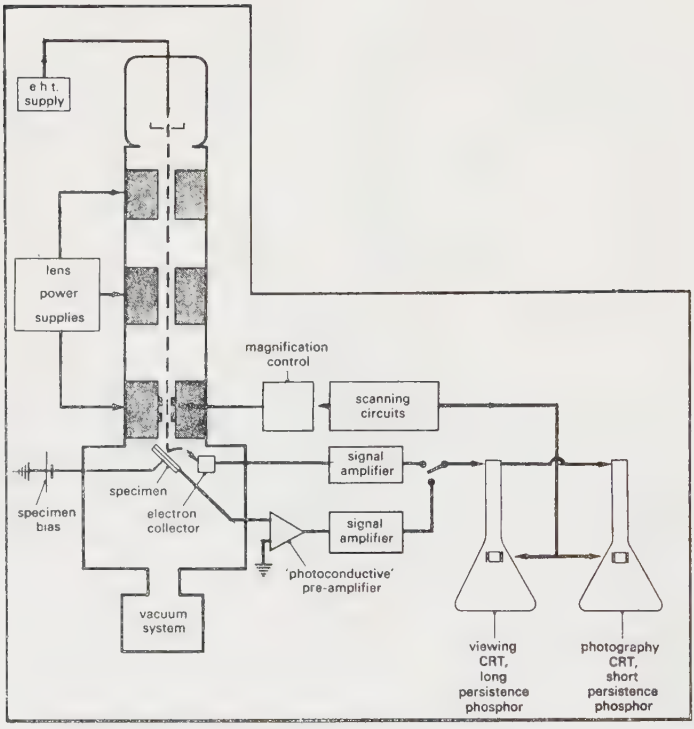

Fig. 3. Block diagram of a Cambridge stereoscan electron microscope.

always better than 500 A, reaching 200 A under the most suitable conditions.

The advantage of this technique is that it is possible to make observations directly on the fractured surface without any further preparation. This also makes it possible to keep the orientation of the specimen under control, and while moving the specimen in the microscope find out suitable areas, e.g. those not covered by corrosion products. Finally, the very great advantage with this kind of microscope is the large depth of focus, which makes it specially suitable for studies of very rough surfaces.

The microscope of the Swedish Silicate Institute, Gothenburg, was used for these investigations.

Electron-probe analysis

Corrosion products were analysed by a Cameca electron-probe analyser. Point determinations and scanning technique were used as described by Melford[38] and Kiessling.[39]

Neutron-diffraction investigations

To detect ordering that might occur in the alloy, neutron diffraction studies were made on the pure steels. The specimens were cut into 1 mm^3 pieces, and after heat-treatment at 1050°C for different times, the pieces were radiated in a cylindric specimen holder with 20 mm dia. The effect of the reactor was 30 MV, giving a wave-length of 1.07Å. It was considered that due to the different scattering factors of chromium, nickel and iron, it would be possible to indicate ordered domains in the alloy. The apparatus used at the Swedish Research Councils Laboratory, Studsvik, is described by von Heidenstam.[40]

Resistometric determinations

In addition to electron microscopy and neutron diffraction some resistometric measurements were made to get an average picture of transformation in the steel as a function of temperature. The equipment used was principally a compensator bridge with a sensitive galvanometer as zero instrument and it has been described earlier by Larsson.[41] The sensitivity was within $\pm 10^{-4}$%. The specimen was kept at the proper temperature until a constant value of the resistivity was obtained.

Hardness tests

As the macro hardness usually changes with the degree of ordering, the Vickers hardness was determined on specimens after different heat-treatments.

Planning of the experiments

The specimens were machined from 1 mm thick sheet and then annealed at the proper temperature for the required time. After that they were electrolytically polished, stored in a desiccator for 24 hours and then placed into the stress-corrosion cell and loaded. The electrolyte was heated to boiling temperature in a separate vessel and then poured into the stress-corrosion cell simultaneously as the time counter was switched on and the oxygen inlet opened to the cell.

For investigations of the initial stages the specimen was exposed to the electrolyte for a relatively short time, after which it was withdrawn and a replica made for electron-microscopic investigation. Usually the electron microscopic investigations were followed by optical investigations.

Time to fracture was usually taken as the measure of the sensitivity to stress corrosion. Fractured specimens were investigated in the optical microscope and in the case of electron-microscopic observations they were thinned down from one side. The electron-microscopic observations usually aimed at investigating the crack path and studying the dislocation distribution around the tip of corrosion cracks.

Fracture surfaces were investigated either by replica technique in the electron microscope or by direct studies in a scanning electron microscope.

The corrosion products in the cracks were determined by the electron probe analyser.

RESULTS

First the results from studies on the active sites on the metal surface using an oxidation technique will be considered. It is shown how the distribution of the sites is changed with a change in the applied load. The oxidation results are fundamentally considered in relation to the initiation of the stress-corrosion process.

Then the results of studies of different stages of the stress-corrosion process will be given. By replica and thin-foil studies in the electron microscope the initial stages are followed and by means of optical microscopy the propagation of stress-corrosion cracks are studied.

Finally the results from related studies, as stacking-fault energy, ordering, dislocation distribution and the effect of environment and grain size of the alloy, are summarized.

Active sites on the metal surface and the effect of applied load on the distribution

Unstressed materials. Results from oxidation studies of unstressed material have been summarized earlier in a paper by Rönnquist and Shiels.[1] In this work it was found that oxide nuclei were not necessarily formed on dislocations in the stainless steel. Similar results have also been reported in the case of pure iron studied by the present author and Thomas.[3] In this latter work special care was taken to avoid thermal movement of dislocations during the oxidation process.

Stressed materials. In an earlier paper[2] it was reported that on a fully annealed α-brass the oxide nuclei were randomly distributed on the different grain surfaces, if (a) no load was applied on the specimen. When loaded the distribution of oxide nuclei changed drastically. At stresses below yielding (b) the grain boundaries were heavily attacked and at stresses above yielding (c) the nuclei were located on slip directions.

Similar results were obtained in the case of stainless steel, but the location of nuclei to the slip directions appeared at considerably lower stresses. This was typical of an oxidized specimen in oxygen at elevated temperatures, Fig. 4, and of oxidized specimen in chlorine gas at 120°C, i.e. at the same temperature as the stress-corrosion tests were carried out in the boiling magnesium-chloride solution, Fig. 5.

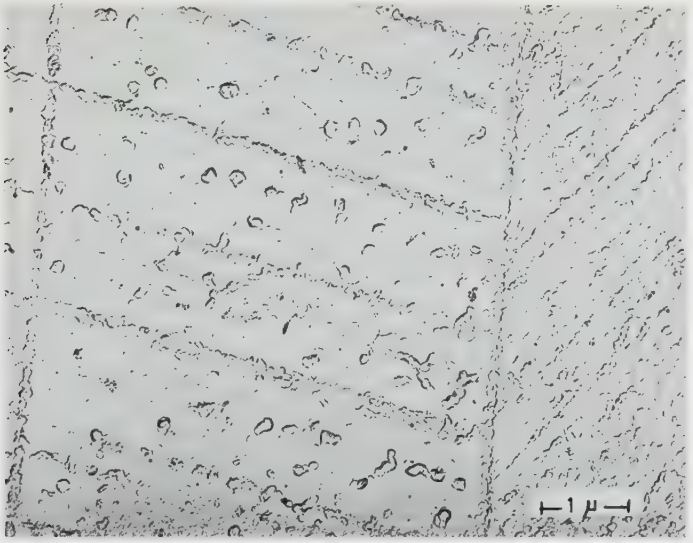

Fig. 4. Electron micrograph of a carbon replica of oxidized 18: 11 steel, oxidized at 300°C, 3 hrs, under stress, amounting to 40% of 0.2% proof stress.

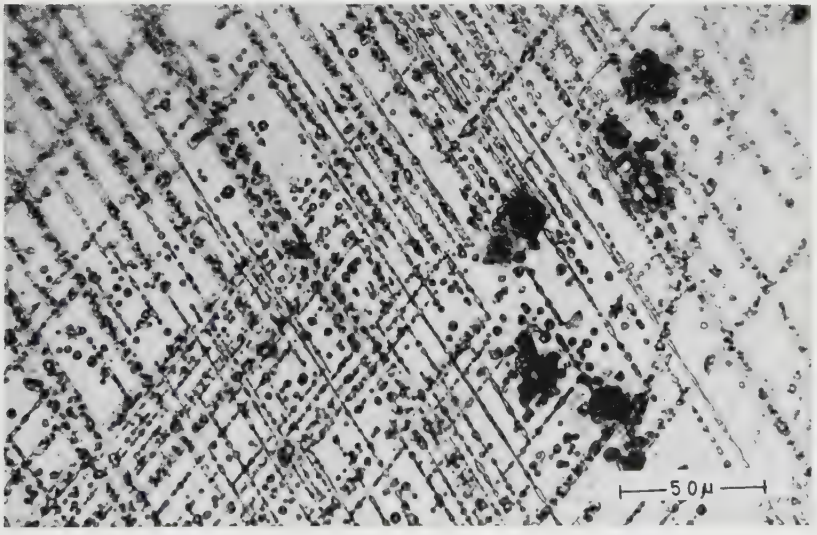

Fig. 5. Optical micrograph of 18: 11 steel, oxidized in Cl_2 at 120°C, 7 hrs, under stress, amounting to 40% of 0.2% proof stress.

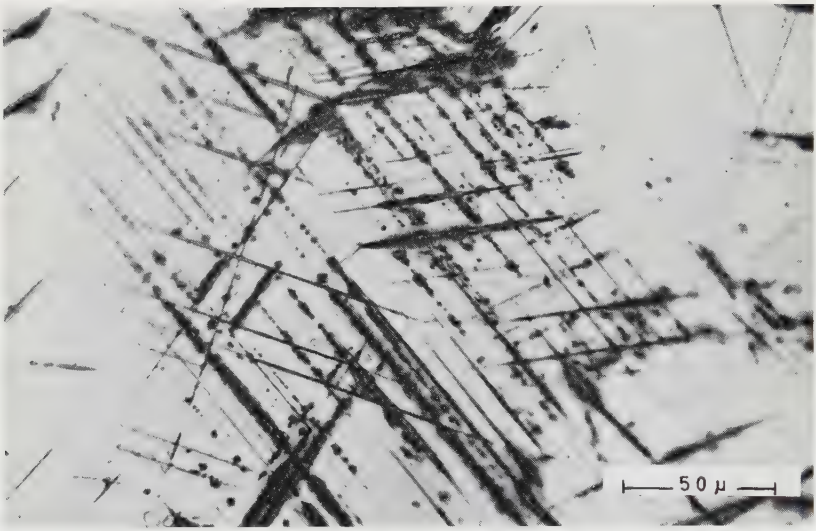

Fig. 6. Optical micrograph of 18: 11-2P steel, stress corroded in 3.5 M $MgCl_2$ solution.

From the oxidation studies it was evident that the reactivity of the grain boundaries was much greater in the case of α-brass than in stainless steel.

Initiation and propagation of stress-corrosion cracks

From the electron-microscopic observations it has been reported earlier that the stress-corrosion process is initiated by pit formation along slip traces on the metal surface.[5] This is in agreement with the oxidation results and it has also in the case of pitting been stated that the pit distribution is random when no load is applied.

During the corrosion process the pits grow, and join up to form micro cracks, Fig. 6.

In the bottom of a macro crack micro cracks are formed. It has been pointed out earlier that the micro cracks are oriented along slip directions in the metal.[5]

It is concluded that during all the different stages of a stress-corrosion process, the slip planes play an important role, especially in the case of stainless steel. In the case of α-brass it has been found that the transgranular cracks are usually initiated at the grain boundaries.

In agreement with Hines[26] it was found that the main direction of stress-corrosion cracks was perpendicular to the applied stress, but they were always close to one of the slip directions of the metal, Fig. 7.

The fractographic studies show that the crack is of a brittle mode when caused by stress corrosion, as seen in Fig. 8. The final stage of

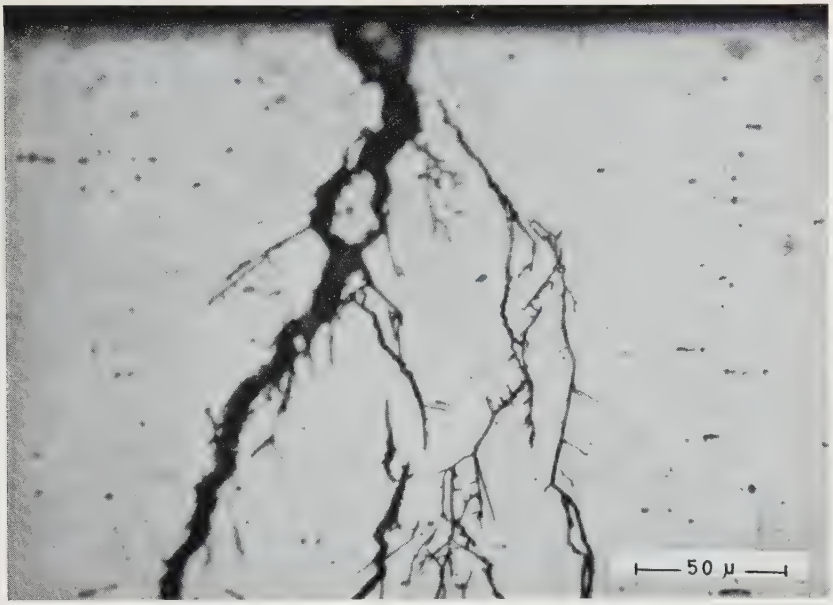

Fig. 7. Optical micrograph of 18: 11 steel with stress-corrosion crack, showing the relation between crack path and metal structure.

the fracture is always, as expected, of ductile type, which is shown in Fig. 9.

In the austenitic-ferritic steel the cracks went through the austenitic grains and when reaching a ferritic grain they bent to follow the grain boundary and then continued, on the other side of the ferritic grain, to became transcrystalline in the austenite again. A typical crack in the duplexstructure steel is shown in Fig. 10.

Stacking-fault energy

In an earlier paper[5] it was reported that phosphorus causes an increase in the sensitivity to stress-corrosion cracking in stainless steel. In phosphorus-free and phosphorus-containing steels the stacking-fault energy was determined by node measurements. No significant difference in the radius of the curved partials was found. (The investigation indicated that the orientation of the nodes in the (111) plane determines to some extent the curvature of the partial dislocation.)

Dislocation distribution around a crack

Thin foils of stress-corroded specimens were prepared by thinning from one side, as described under experimental. The electron-micro-

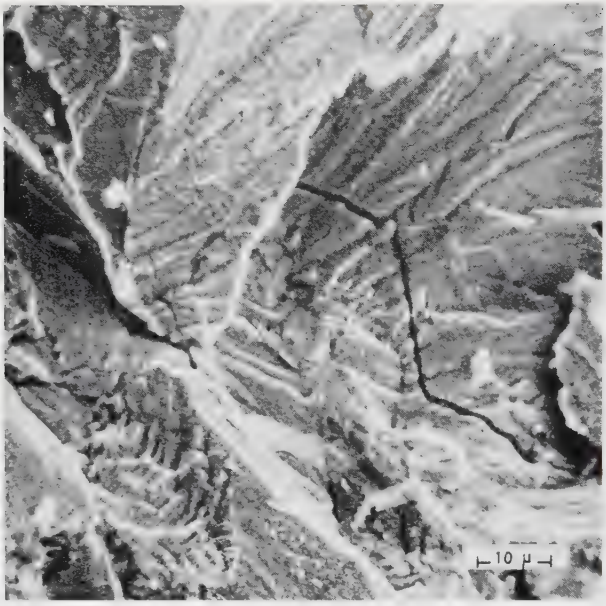

Fig. 8. Electron-scanning micrograph of crack surface of stress-corroded 18: 11 steel, showing the brittle failure.

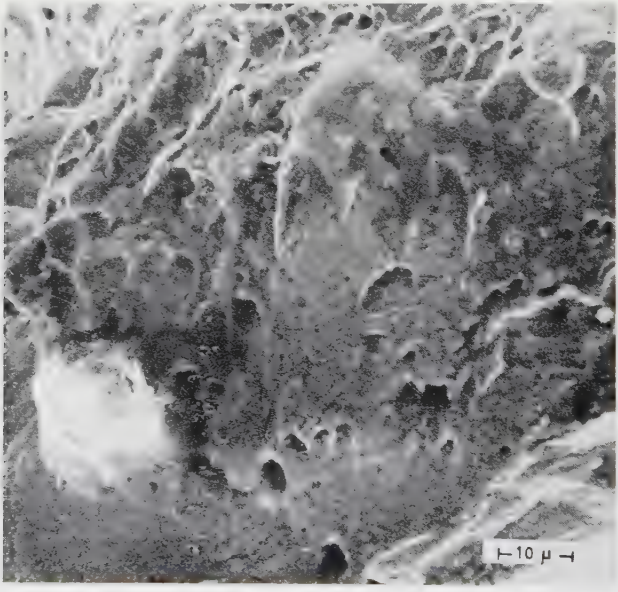

Fig. 9. Electron-scanning micrograph of fracture surface of stress-corroded 18: 11 steel, showing the final stage with ductile failure.

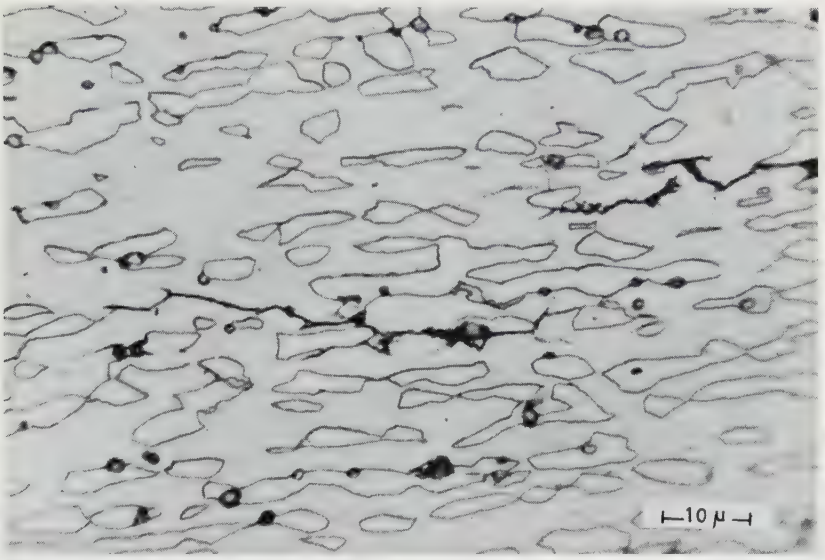

Fig. 10. Optical micrograph of stress-corroded austenite-ferritic steel, showing crack path.

scopic investigations showed that a long dislocation pile-up frequently occurred in front of the crack tip in such specimens, as shown in Fig. 11. A specimen loaded but not attacked by a corroding environment was

Fig. 11. Electron micrograph of a thin foil from stress-corroded 18: 11-2P steel, showing a super-lattice dislocation pile-up in front of a crack.

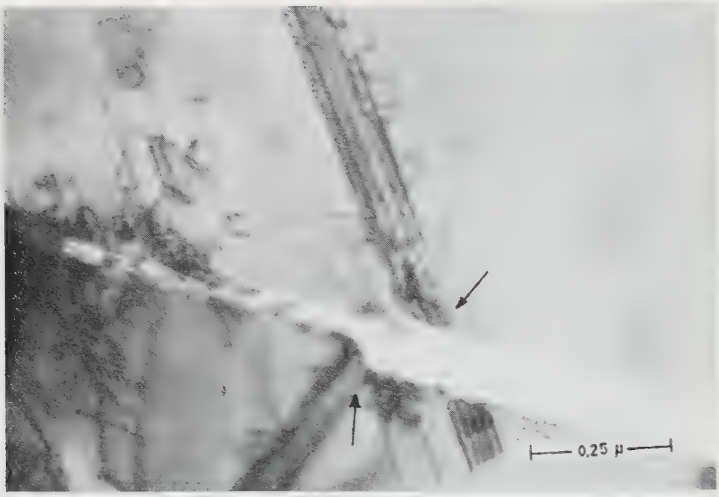

Fig. 12. Electron micrograph of a thin foil from stress-corroded 18: 11-2P steel, showing a slight dissolution of the metal where dislocations reach the crack (indicated by arrows).

investigated by a similar technique. No cracks and dislocation patterns were found in this case. The typical cracks with related dislocations must be the result of the stress-corrosion process.

If a dislocation pile-up was formed along a slip plane not coincident with the main direction of the crack, there was a tendency for branching of the original crack as shown in Fig. 12.

It is concluded that areas containing dislocations are more easily dissolved than dislocation-free areas.

Ordering

According to the review article by Stoloff and Davies,[50] ordering in copper alloys is a rather well-known and extensively investigated phenomenon. However, very little has been done on the iron-chromium-nickel system and it is still uncertain whether or not ordered domains are formed in austenitic stainless steel.

Using thin foil electron microscopy the dislocation configuration was investigated. It was found that some of the dislocation pile-ups mentioned above could be interpreted as super-lattice dislocations (Fig. 11), and dislocation pairing was also observed, Fig. 13. These observations are considered to be evidence for the presence of ordered domains.

To obtain an average picture of the transformation in the alloy, a resistometric curve was determined as a function of temperature. The curve, shown in Fig. 14, is made up of four different parts. The first

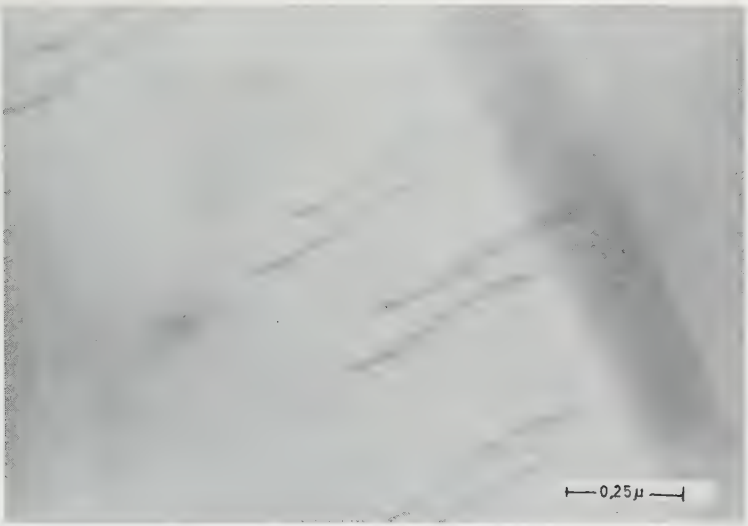

Fig. 13. Electron micrograph of a thin foil from stressed 18: 11-2P steel, showing pairing of dislocations in a super lattice.

change in the linearity is marked by B. This point coincides with the Curie temperature of Ni. The next change, at C, is presumably due to the formation of precipitates, as demonstrated in Fig. 15, a–d. Above 600°C the results could be interpreted as indicating ordering, but they can not be taken as definite evidence. The results from the neutron-

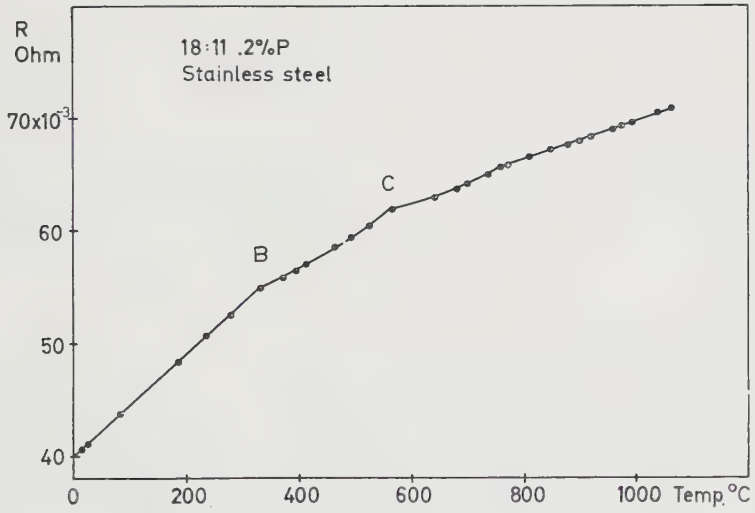

Fig. 14. Resistance of 18: 11-2P steel vs. temperature.

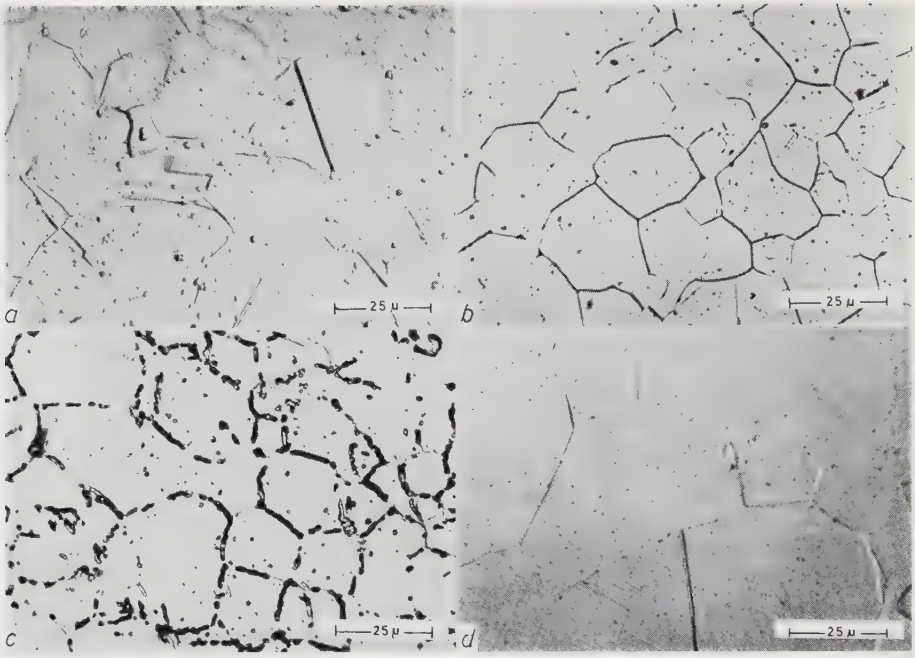

Fig. 15. Optical micrographs of 18: 11-2P steel heat-treated for 150 hrs at a) 450°C, b) 550°C, c) 750°C, and d) 1050°C.

diffraction studies and the hardness tests can be characterized in the same way.

Effect of the environment

It is known from published work on stress-corrosion cracking of α-brass that in ammoniacal solutions the time to fracture is drastically reduced by addition of a copper(II) salt.

In the case of stainless steel, time to fracture was studied at constant load but with different amounts of iron(III) chloride added to the magnesium-chloride solution. The relation between time to fracture and the addition of the $FeCl_3$ is shown in Fig. 16, and it is clear that the time to fracture decreases with increasing concentration of $FeCl_3$.

Influence of the grain size

Time to fracture was determined for specimens of the pure stainless steel with different grain sizes. The corrosion test was carried out in pure magnesium-chloride solution as well as in solutions containing iron(III) chloride. In both types of solutions it was found that time to fracture was smaller for the steel with a bigger grain size than for the steel with smaller grains. The results are presented in Table IV.

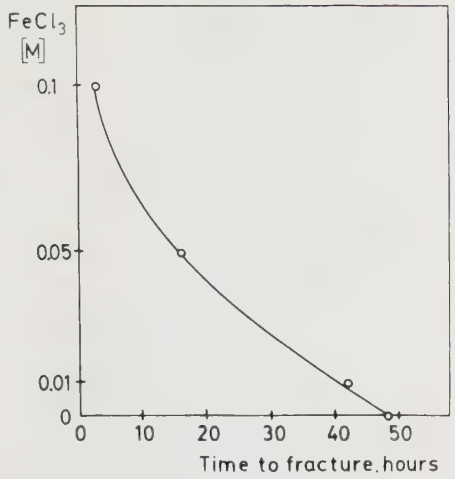

Fig. 16. Relationship between time to fracture of an 18: 11 steel stress-corrosion tested in an $MgCl_2$ solution, and amount of $FeCl_3$ added.

Effect of the applied stress

The time to fracture was taken as a measure of the sensitivity to stress corrosion and was determined as a function of the applied stress. It is obvious from Fig. 17, that the curve showing the change in time to fracture vs. applied stress can be described in three parts. In the first part (I)—the lower range of applied stress—the time to fracture is drastically decreasing with increasing stress, in the second part (II) the time to fracture is nearly independent of stress, and in the third part of the curve (III) there is again a decrease in time with increasing stress.

The transition I II corresponds to the upper limit of the applied stress necessary to activate some dislocation sources, e.g. low angle boundaries and Frank–Read sources.[42] The transition II/III is related to the yielding of the alloy.

TABLE IV. *Influence of grain size on time to fracture. Steel 18:11*

	Tested in $MgCl_2$		Tested in $MgCl_2 + FeCl_2$	
Grain size, ASTM number	2	7.5	2	7.5
Stress, kp/mm^2	12.1	15.7	9.7	12.4
Time to fracture, mean value, h	69	141	4	8

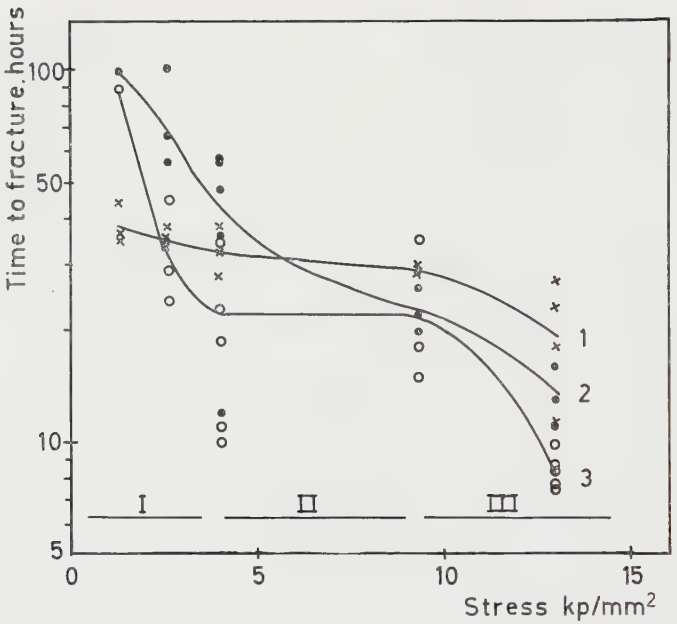

Fig. 17. Time to fracture vs. applied stress for specimens tested in 3.5 M $MgCl_2$ solution. Curve 1 = 18: 8 1 steel (x). Curve 2 = 18: 11-2P steel annealed at 1050°C, 150 hrs (●). Curve 3 = 18: 11-2P steel annealed at 1050°C, 1 hr (○).

Analysis by means of electron-probe analyser

Using the Cameca electron-probe analyser the corrosion products in some cracks were investigated. Fig. 18 shows a typical line-scanning curve of chromium when passing a crack in stainless steel. The corrosion products formed on the walls of the cracks mainly contained compounds of chromium.

Values from point determinations gave 41% Cr, 5% Fe and 1% Ni. Due to the porous structure of the corrosion layer the scatter in analysis values was unusually large, but the figures are given to show the internal relations between the alloying elements. Often Fe and Ni were present in the products, but only to a very low percentage.

No signs of increased concentration of any alloying element to the metal surface of the crack sides could be detected by the micro-probe technique.

INTERPRETATION AND DISCUSSION OF THE RESULTS

Before going into a detailed discussion, a few data in the literature which must fit into a final theory will be pointed out. In the introduction the work of Hore and his co-workers was mentioned.[23, 25] One of the most

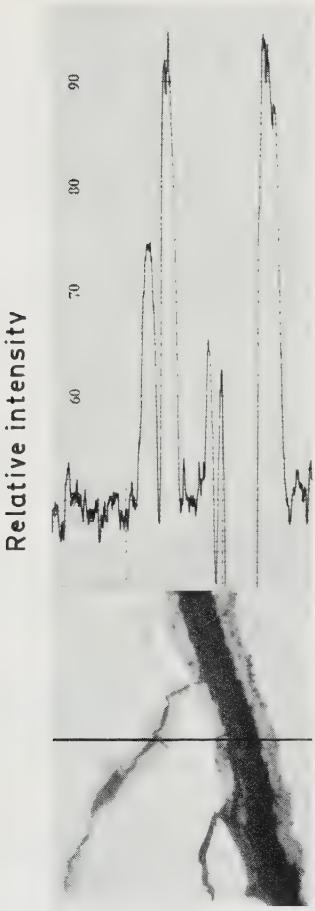

Fig. 18. Record of intensity of chromium line (upper part) obtained in scanning specimen with cracks as shown by line (lower part).

important points in their observations was the effect of yielding rate on the anodic dissolution. A static metal is dissolved by a far lower rate than a metal during yielding.

Pickering and Swann,[33] who studied the dislocation configuration in different alloys, stated that a coplanar dislocation arrangement is essential for the sensitivity to stress corrosion. A coplanar arrangement is achieved when cross slipping of dislocations does not easily occur. Factors causing a restricted slip of dislocations are for instance low stacking-fault energy and ordering.

There are different opinions about the cracking mechanism, but all authors agree that an electrochemical dissolution is involved in the

cracking process. This is strongly supported by the fact that the cracking process is prohibited by anodic protection.

It has already been pointed out that stress-corrosion attack occurs as a brittle failure in a ductile metal. For a long time it has been thought that stress corrosion cracks appear only in alloys. Recently, however, cases of stress-corrosion cracking of pure copper have been reported by Pugh, Montague and Westwood.[43] Both transcrystalline and intercrystalline cracks were observed.

The stress-corrosion phenomenon is a complex problem, mainly because not only the properties of the metal are essential, but also the properties of the corroding environment. As mentioned above stress-corrosion cracking is caused by specific electrolytes. Copper alloys crack in ammoniacal solutions, while austenitic stainless steels crack in chloride solutions with a transcrystalline failure. None of the theories fully explains all these characteristics, which are essential for stress-corrosion failure.

In the present paper a model for the stress-corrosion process is suggested, which is able to explain not only the physical side but to a great extent also the chemical side. The different stages of the process which will be discussed are initiation, involving pit formation and formation of micro cracks, and propagation, involving chemical dissolution at the tip of the crack. It is suggested that crack formation is promoted by (1) the free energy from the chemical dissolution, (2) the dislocation concentration at the tip of the crack and (3) the sorption of metal complexes from the corroding environment.

Initiation of stress-corrosion cracks

For specimens under varying stresses in $MgCl_2$ solutions Hoar and Hines[27] have found typical curves for the potential as a function of time, Fig. 19. The suggested explanation of the form of the curve is as follows: In the range A–B the potential drop results from the penetration of the solution into pores and cracks in the oxide film, and anodic dissolution of the metal begins. In B–C the rise in potential is caused by a film-repair mechanism based on formation of precipitates of hydroxide or oxide and in C–D a film break-down condition has been established. Further, Hoar and Hines report that there is a long incubation period before cracking is initiated and Banartt *et al.*[44] in agreement with this state that an appreciable period of corrosion is usually necessary before the first crack appears.

From the present work it is obvious that the incubation period does not only involve a general corrosion, but also the formation of etch pits along the slip directions on the metal surface. This is in agreement with simultaneously reported observations by Swann and Embury[34] and Louthan.[48]

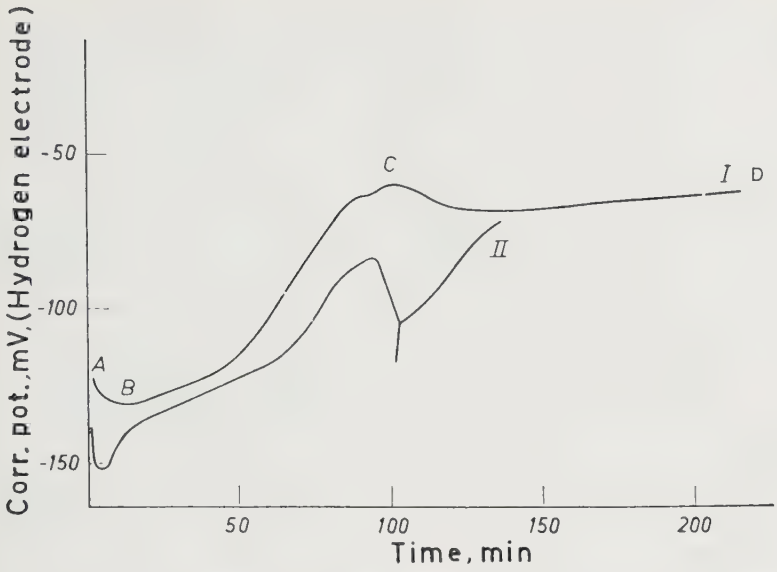

Fig. 19. Corrosion potential (hydrogen electrode) vs. time. Curve I = unstressed specimen. Curve II = stressed specimen.

The distribution of the active sites on the metal surface has been shown to be highly affected by the mechanical conditions. A stress-free specimen shows a random distribution of active sites while a stressed specimen shows a deposition of the reaction products on definite crystallographic directions on the metal surface. It is suggested that the reaction at the slip planes is caused by the presence of moving dislocations reaching the metal surface. The high activity of moving dislocations is demonstrated by the observations made on oxidized thin foils. No significant evidence could be found of oxide nuclei on static dislocations. This was typical of pure iron as well as of austenitic stainless steel.[1, 3]

Formation of etch pits along slip directions seems to be essential, but they must not necessarily be formed during the very first stage of the process. Many authors have found that if a specimen is corroded without applied stress in the beginning of the process, the time to fracture will not drastically change. This may be taken as an evidence for the necessity of a general corrosion during the initial stages. As far as the suggested effect of complexes in the environment is concerned, an essential reaction during the incubation period must be the formation of metal ions.

Propagation of the stress-corrosion crack

A weak point in a pure electrochemical theory is the omission of any consideration of the detailed properties of the stress-corroded metal.

According to such a theory one would expect every metal to crack. A historical event in the development of the stress-corrosion theory was the discovery by Hore and Hines of the effect of yielding on the corrosion rate. By this discovery a bridge was built between the electrochemists and the metal physicists. The fact that a yielding metal is less nobel than a static one gives an explanation to the observation that slip planes might be more active than other areas of the metal surface. Every dislocation reaching the surface causes local yielding of the metal. Near a notch, such as an etch pit, there will be a higher concentration of stress than at some distance from it. The region with the higher stress will be favourable for activation of dislocation sources.

It was also found in the present work that the tip of a corrosion crack was often connected with a path in front of the crack containing dislocation pile-ups. Due to the high velocity of the dislocations, compared with the movement of an electrochemical reaction front, it is reasonable to assume that the dissolved metal mainly consists of the disturbed regions surrounding the dislocations moving into the tip of a crack. Assuming this, the strain energy of the dislocation and the free energy of the chemical reaction will be available for formation of the crack. However, as will be shown, these energies are not large enough to break the metal-metal bonds. By assuming that there is a sorption of complexes, formed between one of the alloying elements and ions in the corroding medium, on the free metal surface at the tip of the crack, it is reasonable to assume that the sorption reduces the energy required to break the metal-metal bonds. The three main features suggested in the model—effects of dislocation configuration, chemical reaction and sorption of the complexes—will be further discussed.

Dislocation configuration

Since 1959, when Swann and Nutting[45] published the evidence of attack on stacking faults in a thin foil of brass, a number of papers on the influence of stacking-fault energy on stress-corrosion cracking have appeared.[4, 5, 46–48] The subject is reviewed by Parkins,[15] among others. Swann and Nutting suggested that the preferential attack on stacking faults was due to the stress concentration associated with the slots formed. However, in a later paper it is suggested that the stacking faults determine the dislocation configuration.[46] As the stacking faults restrict cross slipping, a low stacking-fault energy causes a planar arrangement of the dislocations, which determines the morphology of the stress-corrosion attack.

Tromans and Nutting[49] concluded recently that the mechanism for stress-corrosion initiation is basically the same for both intergranular and transgranular modes of failure. Failure occurs at regions with high

local dislocation densities. These regions are at the grain boundaries in the case of intergranular cracking and at dislocation pile-ups in the case of transgranular cracking.

Further, Tromans and Nutting pointed out, a prerequisite to stress-corrosion cracking being the segregation of solute atoms to the dislocations, the chemical reactivity of these regions will change. Transgranular cracking will occur only in alloys of low stacking-fault energy, e.g. less than 20 ergs/cm^2, where extensive dislocation pile-ups are likely to form. Increasing the amount of plastic strain in such alloys produces more pile-ups and increases the tendency for transgranular cracking to occur.

In the present model it is suggested that a restricted slip of dislocations is essential for stress-corrosion cracking. A dislocation source can deliver dislocations continuously to the tip of a crack only when the source is on a slip plane through the tip. A coplanar arrangement is obtained in alloys with low stacking-fault energy or with a certain degree of ordering.

Stacking-fault energy

Node measurements have often been mentioned as a suitable method for determining stacking-fault energy when the fault energy is low, and a number of measurements relating to stress-corrosion cracking have been carried out, using this method. Most of the values appearing in the literature are based on a limited number of measurements, and the reliability of fault-energy values has been unknown. A factor which has usually been neglected is the effect of orientation of the dislocation node in the (111) plane. In an earlier paper[4] a systematic correlation between the radius of the curved partials and their orientations in the slip planes was found.

As it has been suggested that a coplanar dislocation arrangement favours the sensitivity to stress corrosion, one would expect that sensitive alloys should have a low stacking-fault energy. This does not always seem to be true, however. The contradictory situation concerning the suggested relation between stacking-fault energy and sensitivity to stress corrosion might partly be explained by the uncertainty of the fault-energy measurements, which are often based on only a few measured nodes. It has been shown earlier[4] that the radius for one steel varies from 300 to 2800 Å, due to the different orientations of the nodes.

It has been reported that alloys with low stacking-fault energy do not always show a coplanar dislocation arrangement, as one would expect. However, it must be pointed out that at higher degrees of deformation the dislocations might move out of their slip-planes and cause a tangular cell structure. On the other hand, alloys with a high stacking-fault

energy might show a coplanar arrangement if a certain degree of ordering is present. On this basis a coplanar arrangement might still be a good characteristic for a metal sensitive to stress-corrosion cracking.

Ordering

It was mentioned above that in addition to a low stacking-fault energy, ordering might be a factor determining the distribution of dislocations during a deformation process. The influence of ordering has been studied by Pickering and Swann[33] and Douglass, Thomas and Roser.[46] A number of papers dealing with the mechanical properties and ordering have appeared during the last years, and are critically reviewed by Stolof and Davies.[50] Very little work has been done on iron, chromium and nickel systems except that mentioned above. Beel, Roser and Thomas[51] made a diffraction analysis of dislocation pairs for detecting order in solid solutions. They conclude from the observations of super dislocations that ordering is present in stainless steel, and particularly near the $(Fe, Cr)_3N$ composition. The results confirm earlier suggestions that short-range order exists in these alloys and that ordering is responsible for the observed increases in stacking-fault energy.[46]

In the present work ordering was studied by means of electron microscopy and resistometric determinations. The variations of the resistivity with annealing time and temperature can not wholly be explained by the metallographically observed phase changes (Figs. 14 and 15). The steel used was also studied by means of neutron diffraction. However, the scattering factors for the different alloying elements do not differ enough to give a suitable diffraction pattern to indicate a change in ordering. The ordered domains might even be too small to admit detection with this technique. In electron-microscopic studies of thin foils produced by electrolytic thinning from one side of stress corroded material it has frequently been seen that a crack path is located to dislocation pile-ups, which in a few cases have been interpreted as being of the super-lattice type (Fig. 12). The best evidence for ordering is the dislocation pairing observed, as shown in Fig. 13.

Restricted slip of dislocations

In the present model it is assumed that dislocation sources in front of a crack are more easily activated than sources in other areas of the metal. This is due to the higher strain value of the alloy close to the tip of the crack. Dislocations formed in an alloy with coplanar arrangement will preferably move on the same slip plane. So dislocations moving on slip planes ending at the tip of the crack will slip into the crack. The movement of dislocations into the tip of the crack is favoured by the

chemical dissolution of the alloy, because every obstacle in front of the dislocation pile-up will be reduced, and the chemical dissolution will be favoured by the moving dislocations due to the strain field around the dislocation reaching the metal surface. The present results as shown in Figs. 11 and 12 are strong evidences for this suggestion. It is obvious from Fig. 11 that there is a tendency for areas connected to dislocation pile-ups moving into the side of the crack to be dissolved, as shown by the arrows in the figure.

Fig. 17 shows the relation between time to fracture and applied stress. In the lower range of the applied stress there is a sharp change in time to fracture. This has been interpreted as a result of the activation of dislocation sources. The higher the stress, the shorter the time to fracture will be. But when all the dislocation sources are activated which could contribute to the transport of dislocations into the tip of the crack, there will no longer be a change in time to fracture with increasing stress, which is also shown by Fig. 17. At very high loads, when the yield point has been passed, there will again be a rapid change in time to fracture with the applied stress. Summarizing from the same figure it may be said that in the range marked I, dislocation sources are activated and the dislocations are moving into the tip of the crack. In range II no new contributing dislocation sources are activated, and in range III yielding occurs.

It was mentioned above that ordering might favour a restricted slip of moving dislocations, which would obviously also favour stress-corrosion cracking, according to the present model. However, this is not necessarily the only way in which ordering could influence the cracking mechanism. When a dislocation is formed in an ordered structure, it causes by its movement a destruction of the order. As the ordered structure is more stable than the disordered one, a new dislocation will easily form, moving behind the first one, reconstructing the order. In this way when, once a dislocation is formed, another one follows, this process favouring the chemical dissolution.

The fact that the cracks occur in the austenitic structure in the austenitic-ferritic steel is also in good agreement with the suggested model, because in the austenitic phase the dislocations do not cross-slip as easily as in the ferritic (Fig. 10).

Environment

Mattsson[7] showed that transcrystalline cracking in α-brass is typical in ammoniacal solutions. He even showed that the transcrystalline failure was related to definite pH ranges. It is obvious that these ranges coincide with the stability ranges of the copper and zinc-tetra-amin complexes. With pH on the acid side, where the complexes are unstable, trans-

crystalline cracking will not occur, but on the basic side, where the complexes are stable, transcrystalline cracking will occur. It is also typical that when copper sulphate is added to the solution, the time to fracture will decrease drastically. Similar observations have been made in the present work—when ferric chloride is added to the magnesium chloride solution the time to fracture will decrease from 60 hours to about 4 hours, as seen in Fig. 6.

The interpretation of these observations must involve an interaction between the complexes formed and the metal surface; and a suggested hypothesis is based on a coordination of the physical behaviour of the metal and the interaction of the complexes in the solution on the metal surface. The assumption of an effect of the environment on the mechanical behaviour is supported by a number of published data. One of the investigations indicating an effect of a surface-active agent was published by Rehbinder in 1928; and Rehbinder and Wennström observed that the flow of lead, tin and copper sheets under constant load was much faster if small amounts of surface-active agents were present in the hydrocarbon bath in which the metal was immersed. They even reported an effect on both the indentation hardness and tensile properties of metals in various electrolytes. A "Rehbinder effect" was also reported by Benedicks and Ruben,[52] who studied steel in different electrolytes. An extensive review of the effect of environment on mechanical properties of metals is given by Kramer and Demer.[53]

Liquid-metal embrittlement of solid metals is suggested by Westwood and Kamdar[54] to be determined by the reduction of the surface energy. Analogies between stress-corrosion cracking and embrittlement by liquid metals have been considered by Nichols and Rostoker.[55] Coleman, Weinstein and Rostoker[56] investigated the effect of stress-corrosion media on the fracture stresses. From the Stroh equation for brittle fracture they could calculate the surface energy from measured fracture values as a function of the grain size. The surface energy on stainless steel is assumed to be at least 10^3 ergs cm^2, which was reduced to 157 ergs/cm^2 in magnesium-chloride solution. This drastic change in surface energy effected by the magnesium-chloride solution might be taken as evidence of the possibility of explaining stress cracking as a pure embrittlement process. However, it must be borne in mind that it is possible to stop a propagating crack by cathodic protection.

If it is assumed that the active component in the electrolyte is a complex, e.g. $FeCl_4^-$, one will be able to explain the variation in effect with the pH of the solution.[59] One will even be able to explain the variations with different halogenide solutions, as the polarisation of the bond metal-halogenide varies. Good evidence for an effect of an iron complex is the observation that time to fracture will drastically decrease when $FeCl_3$ is added to the $MgCl_2$ solution, as mentioned above.

According to Kaesche[21] the iodide has an inhibiting effect on the dissolution of iron. A similar effect would be expected from the other halogenides. Due to the sizes and the polarisation properties of the ions it is possible to predict the effect of different halogenides. Considering the polarisation factors one would expect iodide to be the most effective after sorption on the metal surface, and when considering the sizes, one would expect, as far as the ions have to compete with oxygene, that chloride should have the best inhibiting effect. Practical experience, however, is that halogenides will accelerate a chemical dissolution. This can only be explained by assuming that the halogenides will form complexes with the iron. In a complex, the bond between the central atom and the ligands will be polarized, and the electrons are attracted to the central atom. The dipolic ligands will behave in quite another way than when acting as single free halogenide ions. The electrons in the metal will be more attracted by the dipolic ion in the complex than by a single halogenide ion.

This suggested difference between halogenides as single and as complex ions is in good agreement with the theory of inhibitors. Hackerman[57] found in his studies of corrosion inhibition that agents with a free pair of electrons were in many cases effective inhibitors, but electron deficient agents could cause an accelerated dissolution of the metal. When studying the effect of iodide, bromide and chloride additions to H_3PO_4 on the dissolution rate of mild steel he found a decrease in all cases.

Hackerman also stated that among the halogenides, the chloride was not as effective as bromide and iodide. This could be explained by the different polarization properties of the ions, but a contributing factor might be the strong complexes which chloride forms with iron.

Energy calculations

In this section the different energy factors will be considered, using a simplified version of the suggested model. The simplification implies calculating only with iron. As far as the metal-metal bond in a steel is concerned this is not an over-simplification, when the similarities between the heat of sublimation for iron, 96.68, chromium, 89.37, and nickel, 98.25 kcal/mol are considered. If it is assumed that iron goes into solution forming Fe^{2+}, that chromium appears as Cr^{3+}, and that nickel gives Ni^{2+}, it is found that the free-energy change for iron is 20.3 and for nickel 11.1 kcal/mol, while for chromium there are no data available. It is probable, however, that chromium tends to form a compound in the solution which should be associated with a free-energy change much greater than that for iron and nickel.

Another important energy term is connected with the strain field of the dislocations moving into the crack. According to Cottrell[58] the strain

energy of a dislocation is about 8 eV for each atom plane threaded by the dislocation line. For a length of the dislocation line corresponding to one mol of atoms, this gives a value of about 22 kcal.

If the energy of the metal-metal bond in the steel is assumed to be about 95 kcal/mol, and 20 kcal/mol are received from the chemical dissolution and the same amount from the strain field of dislocations, there should fail about 55 kcal/mol to break the metal-metal bond. However, due to the decrease in surface energy caused by the environment, from 10^3 to 153 ergs/cm^2, the failing 55 kcal/mol are more than well accounted for.

Conclusion

A suggested model for stress corrosion cracking may be summarized as follows:

1. Etch pits are formed along active slip planes due to dislocations moving out to the metal surface.
2. A stress field is built up close to the pit, maintaining an activation of dislocation sources in this area.
3. Dislocations moving into the the pit (or crack) are chemically dissolved.
4. The free energy changes from the strain energy of the dislocations and from the chemical reactions are large enough to break the metal-metal bond if the interaction between the metal surface and the complexes in the solution are taken into consideration.
5. The general corrosion during the incubation period is assumed to be essential for raising the concentration of metal complexes in the environment.

The model explains the necessity of a specific chemical environment to cause transcrystalline failure. It also explains the necessity of specific physical properties of the metal. The effect of grain size as well as the brittle mode of the failure are predicted by the model. In a wider sense the model might be useful for developing theories for phenomena with similar properties, such as cracking in fatigue and creep.

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INVERKAN AV DISLOKATIONER OCH KEMISK MILJÖ PÅ SPÄNNINGSKORROSION I KUBISKT YTCENTRERADE LEGERINGAR

SAMMANFATTNING

Föreliggande uppsats utgör en sammanfattning av spänningskorrosionsundersökningar som utförts de senaste åren vid Institutet för Metallforskning, Stockholm, och har omfattat studier av initiering och fortplantning av spänningskorrosionssprickor i austenitiskt rostfritt stål. Jämförande undersökningar har utförts på α-mässing.

Metallfysikaliska aspekter har i hög grad dominerat arbetet, och följande experimentella metoder har huvudsakligen använts: ljus- och elektronmikroskopi, fraktografi, mikrosondteknik, resistometri och neutrondiffraktion. Angrepp på stål har framkallats i O_2, Cl_2 och $MgCl_2$-lösningar under varierande mekanisk belastning. På α-mässing har använts, förutom gaserna O_2 och Cl_2, ammoniakaliska lösningar.

Det har påvisats ett samband mellan glidplan i metallen och så väl initiering som fortplantning av sprickor. Fortplantningsriktningen är bestämd av dislokationsbilden framför spetsen av korrosionssprickan. En plan dislokationsfördelning gynnar förloppet och detta påverkas därför indirekt av staplingsfelsenergi och ordningsgrad hos legeringen.

En kemisk miljö där ytaktiva komplex kan bildas mellan joner i lösningen och upplösta metallatomer ur legeringen är spänningskorrosionsbefrämjande om komplexen vid sorption på metallytan försvagar metall-metallbindningen.

På grundval av de erhållna resultaten har en modell för spänningskorrosionsprocessen föreslagits, vilken kan sammanfattas enligt följande:

1. Frätgropar bildas längs glidplanen då dislokationer når metallytan.

2. Ett mekaniskt spänningsfält byggs upp i närheten av gropens botten, vilket underlättar aktivering av dislokationskällor i samma område.

3. Dislokationerna som rör sig mot gropen (eller sprickans spets) löses upp kemiskt.

4. Den fria energiändringen härrörande från det med dislokationen förknippade spänningsfältet och den kemiska reaktionen är tillräckligt stor för att bryta metall–metallbindningar, om hänsyn tages till effekten av komplexens sorption på metallytan.

5. En viktig process under inkubationsperioden för ett spänningskorrosionsangrepp är höjningen av koncentrationen för komplexbildande metalljoner i lösningen.

Den föreslagna modellen kan förklara nödvändiga metallfysikaliska och kemiska förutsättningar för ett spänningskorrosionsangrepp.

References

1. A. Rönnquist & S. A. Shiels, A morphological study of the initial stages of the oxidation of an 18-8 steel and a carbon steel in the temperature range 200–500°C. *Jernkont. Ann. 148 (1964) pp. 714–724.*
2. A. Rönnquist, Glidlinjernas betydelse vid initiering av spänningskorrosionssprickor i α-mässing. En jämförelse med austenitiskt stål. *Jernkont. Ann. 149 (1965) pp. 604–611.*
3. A. Rönnquist & K. Thomas, Nucleation of oxide on thin films of pure iron. *Brit. Corr. J. 1 (1965) pp. 47–50.*
4. A. Rönnquist & D. Dulieu, On the determination of stacking fault energies in austenitic stainless steel by the method of extended node measurements. *Brit. J. Appl. Phys. 15 (1964) pp. 1569–1571.*
5. A. Rönnquist, The influence of phosphorus on the stacking fault energy and the sensitivity to stress corrosion of austenitic stainless steel. *Current corrosion research in Scandinavia. Helsinki 1964, pp. 121–126.*
6. S. Rask, Stress corrosion in copper and copper alloys. A bibliography. *Recent advances in stress corrosion. Bulletin No. 25. Royal Swedish Academy of Engineering Sciences, Stockholm 1961, pp. 81–107.*
7. E. Mattsson, Stress corrosion in brass against the background of potential/pH diagrams for the corroding system. *Recent advances in stress corrosion. Bulletin No. 25. Royal Swedish Academy of Engineering Sciences, Stockholm 1961, pp. 50–56.*
8. G. Lind, Stress corrosion cracking in austenitic stainless steels. Apparatus for testing in high pressure water of high temperature. *Recent advances in stress corrosion. Bulletin No. 25. Royal Swedish Academy of Engineering Sciences, Stockholm 1961, pp. 70–76.*
9. Symposium on stress corrosion cracking of metals. American Society for Testing Materials, Philadelphia 1945.
10. Stress corrosion cracking and embrittlement. Wiley & Sons, New York 1956.
11. Physical metallurgy of stress corrosion fracture. Interscience, New York 1959.
12. First international congress on metallic corrosion, London 1961. Butterworths, London 1962.
13. Second international congress on metallic corrosion, New York 1963. National Ass. Corr. Engrs., New York 1966.
14. A. R. Bailey, The stress-corrosion cracking of brass. *Met. Rev. 6 (1961) pp. 101–142.*
15. R. N. Parkins, Stress-corrosion cracking. *Met. Rev. 9 (1964) pp. 201–260.*
16. A. Rönnquist, Spänningskorrosion i metallegeringar. *Sv. Kem. Tidskr. 78 (1966) pp. 304–320.*
17. U. R. Evans, The corrosion and oxidation of metals. Edward Arnold Ltd., London 1961.
18. V. V. Romanov, Korrozionnoe rastreskivanie metallov. Mašgiz, Moskva 1960. [Translation from Israel program for scientific translations, Jerusalem 1961.]
19. L. L. Shreir, Corrosion. Vol. I and II. George Newness Ltd., London 1963.
20. H. L. Logan, The stress corrosion of metals. John Wiley & Sons, New York 1966.
21. H. Kaesche, Die Korrosion der Metalle. Springer-Verlag, Berlin/Heidelberg 1966.
22. T. P. Hoar & J. G. Hines, The stress-corrosion cracking of austenitic stainless steels. *J. Iron Steel Inst. 182 (1956) pp. 124–143.*
23. T. P. Hoar & J. M. West, Mechano-chemical anodic dissolution of austenitic stainless steel in hot chloride solution. *Proc. Roy. Soc. A 268 (1962) pp. 304–315.*
24. D. van Rooyen, Some aspects of stress-corrosion cracking in austenitic stainless

steels. *First Int. Congress Metallic Corr. Butterworths, London 1962, pp. 309–318.*

25. T. P. Hoar & J. C. Scully, Mechanochemical anodic dissolution of austenitic stainless steel in hot chloride solution at controlled electrode potential. *J. Electrochem. Soc. 111 (1964) pp. 348–352.*
26. J. G. Hines, On the propagation of stress corrosion cracks in metals. *Corr. Science 1 (1961) pp. 21–48.*
27. T. P. Hoar & J. G. Hines, Stress corrosion cracking of austenitic stainless steels in aqueous chloride solutions. *Stress corrosion cracking and embrittlement. Wiley & Sons, New York 1956, pp. 107–125.*
28. A. J. Forty, The metal physics of stress corrosion. *Recent advances in stress corrosion. Bulletin No. 25. Royal Swedish Academy of Engineering Sciences, Stockholm 1961, pp. 22–36.*
29. W. D. Robertson & A. S. Tetelman, A unified structural mechanism for intergranular and transgranular corrosion cracking. *Strengthening mechanisms in solids. American Society for Metals, Cleveland 1962, pp. 217–252.*
30. F. E. Fujita, Dislocation theory of fracture of crystals. *Acta metallurg. 6 (1958) pp. 543–551.*
31. A. N. Stroh, The formation of cracks as a result of plastic flow. *Proc. Roy. Soc. 223 A (1954) pp. 404–414.*
32. A. H. Cottrell, Dislocations and plastic flow in crystals. Clarendon Press, Oxford 1958, p. 170.
33. H. W. Pickering & P. R. Swann, Electron metallography of chemical attack upon some alloys susceptible to stress corrosion cracking. *Second Int. Congress Metallic Corr. National Ass. Corr. Engrs. New York 1966, pp. 128–147.*
34. P. R. Swann & J. D. Embury, Microstructural aspects of stress corrosion failure. *High-strength materials. John Wiley & Sons, New York 1965, pp. 327–362.*
35. H. Modin & S. Modin, Handbok i metallmikroskopering. Meritförlaget, Stockholm 1967.
36. G. Nomarski & A. R. Weill, Application à la métallographie des méthodes interférentielles à deux ondes polarisées. *Rev. Métall. 52 (1955) pp. 121–134.*
37. D. A. Melford, Topography, composition and structure: a survey of some modern metallographic techniques. *Metallography 1963. Spec. rep. 80. Iron and Steel Institute, London 1964, pp. 214–218.*
38. D. A. Melford, Topography, composition and structure: a survey of some modern metallographic techniques. *Metallography 1963. Spec. rep. 80. Iron and Steel Institute, London 1964, pp. 219–229.*
39. R. Kiessling, Elektronmikrosonden, ett viktigt mikroanalytiskt hjälpmedel. *Jernkont. Ann. 144 (1960) pp. 847–854.*
40. O. von Heidenstam, Mätningar vid installation av utrustning för neutrondiffraktion. Swedish Research Council's Laboratory, Studsvik, Sweden, and University of Uppsala, Chem. Inst. dep. LF-12, 1965.
41. L.-E. Larsson, Åldringsfenomen i utspädda Al-Mn-legeringar. *Jernkont. Ann. 147 (1963) pp. 617–634.*
42. A. H. Cottrell, The mechanical properties of matter. John Wiley & Sons, London 1964, p. 279.
43. E. N. Pugh, W. G. Montague & A. R. C. Westwood, Stress-corrosion cracking of copper. *Corr. Science 6 (1966) pp. 345–346.*
44. S. Barnartt, R. Stickler & D. van Rooyen, Stress-corrosion cracking mechanism in purified 16% Cr–20% Ni stainless steels. *Corr. Science 3 (1963) pp. 9–16.*
45. P. R. Swann & J. Nutting, Stacking faults and the failure of alloys in corrosive media. *J. Inst. Metals 88 (1959/60) pp. 478–480.*
46. D. L. Douglass, G. Thomas & W. R. Roser, Ordering stacking faults and stress

corrosion cracking in austenitic alloys. *Second Int. Congress Metallic Corr. National Ass. Corr. Engrs. New York 1966, pp. 66–79.*

47. P. R. Swann, Dislocation substructure vs. transgranular stress corrosion susceptibility of single phase alloys. *Second Int. Congress Metallic Corr. National Ass. Corr. Engrs., New York 1966, pp. 188–199.*
48. M. R. Louthan Jr., Stress corrosion cracking of type 304 stainless steel. AEC research and development report DP-907. Savannah River Laboratory, Aiken, South Carolina, 1964.
49. D. Tromans & J. Nutting, Electron microscope studies of stress corrosion cracking. *Fracture of solids. John Wiley & Sons, New York 1963, pp. 637–655.*
50. N. S. Stoloff & R. G. Davies, The mechanical properties of ordered alloys. *Progr. Materials Science 13 (1966) pp. 1–84.*
51. W. Bell, W. R. Roser & G. Thomas, Diffraction analysis of dislocation pairs for detecting order in solid solutions. *Acta metallurg. 12 (1964) pp. 1247–1253.*
52. C. Benedicks & G. Ruben, Bestämningar av vätskors inflytande på hållfasthet, särskilt för glas och härdat stål. *Jernkont. Ann. 129 (1945) pp. 37–106.*
53. I. R. Kramer & L. J. Demer, Effects of environment on mechanical properties of metals. *Progr. Materials Science 9 (1961) pp. 133–199.*
54. A. R. C. Westwood & M. H. Kamdar, Concerning liquid metal embrittlement, particularly of zinc monocrystals by mercury. *Phil. Mag. 8 (1963) pp. 787–804.*
55. H. Nichols & W. Rostoker, Analogies between stress-corrosion cracking and embrittlement by liquid metals. *Trans. Am. Soc. Metals 56 (1963) pp. 494–507.*
56. E. G. Coleman, D. Weinstein & W. Rostoker, On a surface energy mechanism for stress-corrosion cracking. *Acta metallurg. 9 (1961) pp. 491–496.*
57. N. Hackerman, Inhibition of corrosion. [Transcript of lecture.] US Trade Center, Stockholm 1967.
58. A. H. Cottrell, Dislocations and plastic flow in crystals. Clarendon Press, Oxford 1958, p. 38.
59. B. Andersson, Study of stainless steel stress-corrosion cracking by potential measurements. *Corrosion 18 (1962) pp. 425 t–432 t.*